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Hosts of hydrogen in Allan Hills 84001: Evidence for hydrous martian salts in the oldest martian meteorite?

JOHN M. EILER[1]*, NAMI KITCHEN[1], LAURI LESHIN[2] AND MELISSA STRAUSBERG[1]

[1]Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125, USA
[2]Department of Geological Sciences, Arizona State University, Tempe, Arizona 85287-1404, USA
*Correspondence author's e-mail address: eiler@gps.caltech.edu

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Abstract–The martian meteorite, Allan Hills (ALH) 84001, contains D-rich hydrogen of plausible martian origin (Leshin *et al.*, 1996). The phase identity of the host(s) of this hydrogen are not well known and could include organic matter (McKay *et al.*, 1996), phlogopite (Brearley, 2000), glass (Mittlefehldt, 1994) and/or other unidentified components of this rock. Previous ion microprobe studies indicate that much of the hydrogen in ALH 84001 as texturally associated with concretions of nominally anhydrous carbonates, glass and oxides (Boctor *et al.*, 1998; Sugiura and Hoshino, 2000). We examined the physical and chemical properties of the host(s) of this hydrogen by stepped pyrolysis of variously pre-treated subsamples. A continuous-flow method of water reduction and mass spectrometry (Eiler and Kitchen, 2001) was used to permit detailed study of the small amounts of this hydrogen-poor sample available for study. We find that the host(s) of D-rich hydrogen released from ALH 84001 at relatively low temperatures (~500 °C) is soluble in orthophosphoric and dilute hydrochloric acids and undergoes near-complete isotopic exchange with water within hours at temperatures of 200 to 300 °C. These characteristics are most consistent with the carrier phase(s) being a hydrous salt (*e.g.*, carbonate, sulfate or halide); the thermal stability of this material is inconsistent with many examples of such minerals (*e.g.*, gypsum) and instead suggests one or more relatively refractory hydrous carbonates (*e.g.*, hydromagnesite). Hydrous salts (particularly hydrous carbonates) are common on the Earth only in evaporite, sabkha, and hydrocryogenic-weathering environments; we suggest that much (if not all) of the "martian" hydrogen in ALH 84001 was introduced in analogous environments on or near the martian surface rather than through biological activity or hydrothermal alteration of silicates in the crust.

INTRODUCTION

Geological evidence suggests that liquid water has flowed on the martian surface (Baker *et al.*, 1992; Malin and Edgett, 2000), raising the possibility that aqueous geochemical processes and/or biological activity characteristic of the Earth's surface have also occurred on Mars. Hydrogen-bearing phases in martian materials can constrain the environmental conditions and geological settings of the interactions of water and rock on Mars. The "martian" meteorites, including the shergottites, nahklites, Chassigny (collectively the SNCs) and Allan Hills (ALH) 84001, are believed to be the only samples of Mars currently available for laboratory investigation (McSween and Treiman, 1998). However, the possibility of terrestrial contamination of these samples is high; for this reason, studies of putative martian hydrous phases in these rocks must test for properties that are distinctive of martian near-surface materials and therefore indicative of martian processes. D/H ratios of martian atmospheric gases are strongly elevated with respect to terrestrial compounds (Owen *et al.*, 1988) and therefore have the potential to provide such a test.

Previous studies of the mineralogy of martian meteorites Nahkla, Lafayette, Shergotty, Chassigny and Elephant Moraine A79001 found hydrous minerals that likely formed during low-temperature aqueous alteration, including gypsum and other salts, iron-oxy-hydroxides, clays, and serpentine (McSween and Treiman, 1998, and references therein; Bridges and Grady, 2000). All of these samples but one—Chassigny—evolve D-rich water (δD_{SMOW} >> 0‰) on heating to moderate temperatures (600–1000 °C), suggesting that some or all of their hydrous phases formed on the martian surface or in the martian crust (Leshin *et al.*, 1996). A similar vacuum-heating experiment conducted on ALH 84001, an unusually old (4.5 Ga) orthopyroxenite member of the martian meteorite group, is puzzling because it also yielded D-rich water (δD up to +783 ± 20‰) on heating to this temperature range, but microscopy studies reveal only trace hydrous phases, none of which can be confidently identified as the host of D-rich

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hydrogen (Mittlefehldt, 1994; Treiman, 1995; Brearley, 2000). Therefore, the environmental significance of "martian" hydrogen in this sample is unclear.

One possibility is that D-rich hydrogen in ALH 84001 is hosted by organic matter previously recognized in the form of polycyclic aromatic hydrocarbons (PAHs; Becker *et al.*, 1997; McKay *et al.*, 1996), amino acids (Bada *et al.*, 1998), and (more ambiguously) microstructures that are inferred to be composed of kerogen or other non-volatile organic compounds (McKay *et al.*, 1996). These materials have been interpreted either as evidence of martian organic matter (McKay *et al.*, 1996) or terrestrial contamination (Becker *et al.*, 1997; Bada *et al.*, 1998; Jull *et al.*, 1998); their association with D-rich hydrogen would provide some of the strongest possible evidence for their martian origin. Ion microprobe studies found that concretions of carbonate and oxide minerals in ALH 84001 contain unknown but possibly large concentrations of hydrogen (estimated about 1–3 wt% as H_2O) that is often D-rich (up to +1500‰) (Boctor *et al.*, 1998; Sugiura and Hoshino, 2000). However, carbonate concretions are only known to contain nominally anhydrous minerals, including rhombohedral Ca-Fe-Mg-Mn carbonates, magnetite, and iron-sulfide, and veins or blebs of H-poor feldspathic glass. Therefore, these data require the presence of an as-yet unidentified constituent(s) of carbonate concretions—and possibly other portions of this sample—that are hydrogen-rich and high in D/H ratio. PAHs and putative kerogen-rich films are associated with carbonate concretions (McKay *et al.*, 1996), further supporting organic matter as a plausible candidate for this cryptic, D-rich phase. Finally, recent transmission electron microscope (TEM) studies of ALH 84001 have found grains of phlogopite associated with carbonates (Brearley, 2000). These grains are small (~10 nm), rare and have only been identified in disrupted and partially decomposed aggregates of carbonate that form "xenoliths" in veins of feldspathic glass; therefore it is unclear whether they could host a significant fraction of the D-rich hydrogen in the rock or what relationship they have to hydrogen in relatively pristine carbonate concretions. Brearley (2000) suggests that phlogopite is produced by shock metamorphism of an as-yet unidentified precursor hydrous phase in carbonate concretions.

We describe here measurements of the abundance and D/H ratio of water released during low-temperature (≤750 °C) stepped-pyrolysis of untreated and variously pre-treated fractions of ALH 84001. These pre-treatments include: exposure to weak acids (10% and 1 molar HCl and 102% H_3PO_4); exposure to base (a mixture of equal proportions 2 molar NaOH and 30% H_2O_2); heating for ~1 day under vacuum at 150 °C; or exposure to isotopically labeled water ($\delta D = -428.0‰$) at temperatures from 25 to 300 °C. These experiments constrain thermal stability, kinetics of thermal decomposition, kinetics of isotopic exchange, and solubility in acid, base and water of high and low D/H hydrous phases in this rock. Our results can be compared to the known properties of various classes of candidate phases (*e.g.*, phyllosilicates, organic matter, zeolites, *etc.*) in order to restrict the possible set of hosts for this hydrogen. However, we note that our data do not provide strict phase identification, which will require further studies using methods with detailed structural specificity (*e.g.*, electron or Raman microscopy).

SAMPLES AND METHODS

Two subsamples of ALH 84001 were used in this study: One fragment of split ALH 84001.68 weighing ~2 g was obtained from E. M. Stolper and a second weighing ~50 mg from split ALH 84001.305 was also studied. Both samples were gently crushed into centimeter- to millimeter-sized fragments by striking with a stainless steel mortar previously cleaned with ethanol. Individual fragments (generally weighing on the order of 10 mg) were hand picked under a binocular microscope, preferentially selecting pieces that visually appeared to be poly-granular and representative of the bulk in terms of color and abundance of easily identified constituents (chromite, glass, pyroxene and macroscopic carbonate). Each individual fragment was then gently crushed a second time to a grain size of ~0.1 mm and all of the crushed material either immediately subjected to a stepped-heating experiment or pre-treated as described below and then subjected to a stepped-heating experiment.

We describe the details of pre-treatments performed for each experiment in the context of experimental results in the following section; procedures and materials that are common to several pre-treatments are as follows: acid and base etches were conducted by placing the sample and reagent in Teflon™ vessels sealed by a screw-on Teflon™ cap and heating those samples on a hot plate at 25 to 80 °C for from several hours to 2 days. Exposure of the sample to isotopically labeled water was conducted by placing the sample in a Pyrex™ tube, attaching that tube to a vacuum line (~10^{-7} bar baseline pressure), cryogenically transferring ~10^{-4} moles of isotopically labeled water into the sample tube, flame sealing the tube under vacuum and heating in a furnace at 25 to 300 °C for several hours to 4 days. Vacuum heating pre-treatment was conducted in a similar fashion, but when the sample was attached to the vacuum line it was heated to 150 °C using a resistance furnace overnight (16 h) while maintaining a baseline pressure of ~10^{-7} bar. Reagents used in these experiments include: 10% and 1 molar HCl prepared from de-ionized water and 6 normal reagent-grade HCl; 102% H_3PO_4 prepared from vacuum boiling of reagent-grade 85% H_3PO_4; reagent-grade 30% H_2O_2; reagent-grade 2 molar NaOH; and standard light Antarctic precipitation (SLAP) distributed by the International Atomic Energy Agency.

Conventional hydrogen isotope analysis of water poor materials such as ALH 84001 requires ~1 g per measurement and is relatively challenging even at this size (Leshin *et al.*, 1996). We conducted several dozen separate stepped-heating experiments on treated and untreated portions of this rock;

therefore, our study would have required a prohibitively large fraction of this small (~10 to 15 cm diameter), precious sample had we used conventional methods. For this reason, we instead used an analytical method involving stepped heating, reduction of evolved water, and mass spectrometry of product H_2 in a continuous stream of He (Eiler and Kitchen, 2001); Fig. 1 schematically illustrates the principle components of the apparatus used for these measurements. This method reduces the sample size for hydrogen isotope analysis by several orders of magnitude compared to conventional techniques, such that detailed stepped-heating experiments can be conducted on just a few milligrams of water-poor materials (or tens of micrograms of water-rich materials). Briefly, this method involves the following procedure: (1) samples are loaded in a horizontal 1/4" O.D. silica glass or alumina tube and heated overnight at ~50 °C under a He flow of about 30–50 cc/min; (2) a movable resistance heater positioned over an empty portion of the sample tube is cycled in temperature from 25 to 750 °C one or more times and the blank determined by collecting and analyzing water from the sample tube every 3 to 5 min using methods summarized below; (3) the resistance heater, held at a temperature of 250 °C, is slid over the portion of the silica glass tube holding the sample and heated to 750 °C in several steps over a period of ~30 to 120 min; water evolved from the sample tube into the He stream is cryogenically collected in a capillary of deactivated fused silica and periodically (every 2 to 5 min) purged through a reduction furnace where it is converted to CO and H_2, which are swept into the source of a gas source mass spectrometer and the HH^+ and HD^+ simultaneously detected as brief, time-varying signals.

The analytical method we used has an accuracy and precision for water molarity of approximately 5 to 10% relative, and an accuracy and precision for D/H of approximately 2–3‰ (Eiler and Kitchen, 2001). The chief uncertainties in these measurements for an application such as that described here come from blank corrections, which vary from negligible (<1% of recovered water) in the first few minutes of a given temperature step to almost complete dominance of the water collected at the end of that temperature step. Blanks are generally reproducible in both size (about ±5% relative) and isotopic composition (about ±2 to 5‰) during a given analytical session and therefore can be subtracted from sample measurements with relative confidence. All δD values are reported with 1σ error bars calculated by Monte Carlo methods based on observed reproducibility of both the size and isotopic composition of blanks; the size of the blank for each experiment is indicated with horizontal dashed lines in Figs. 2 and 3. The

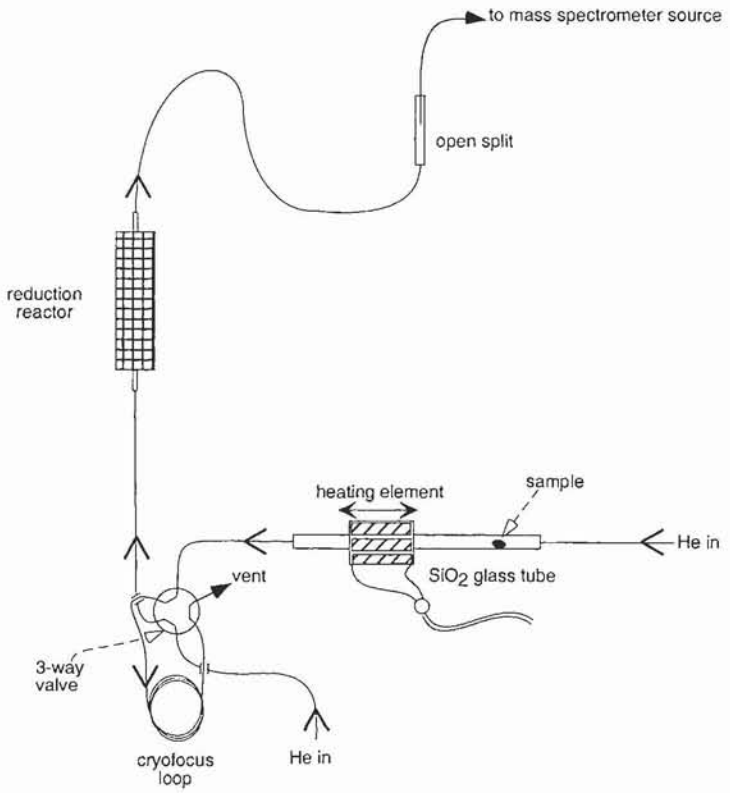


FIG. 1. Schematic illustration of apparatus used for sample heating, on-line water reduction and mass spectrometry; some components are omitted for simplicity. See Eiler and Kitchen (2001) for details. Fine solid lines are fused-silica capillaries. "V"-shaped arrows indicate the direction of He flow through the apparatus. The position of the three-way valve can be rotated 60° clockwise to reverse the direction of He flow through the cryofocus loop, purging collected water from the loop and into the reduction reactor. The heating element can be slid horizontally over the SiO_2-glass tube, as shown.

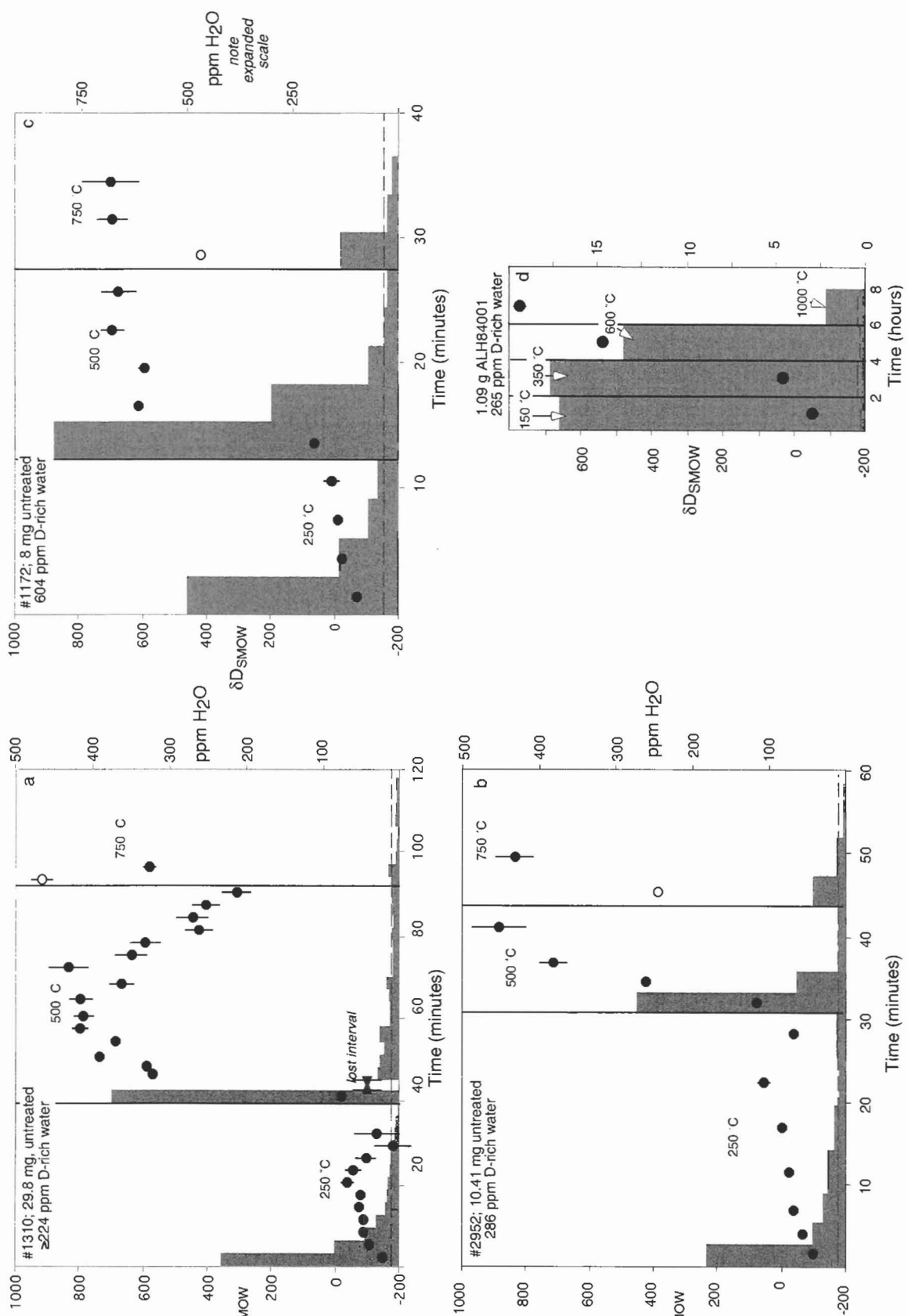
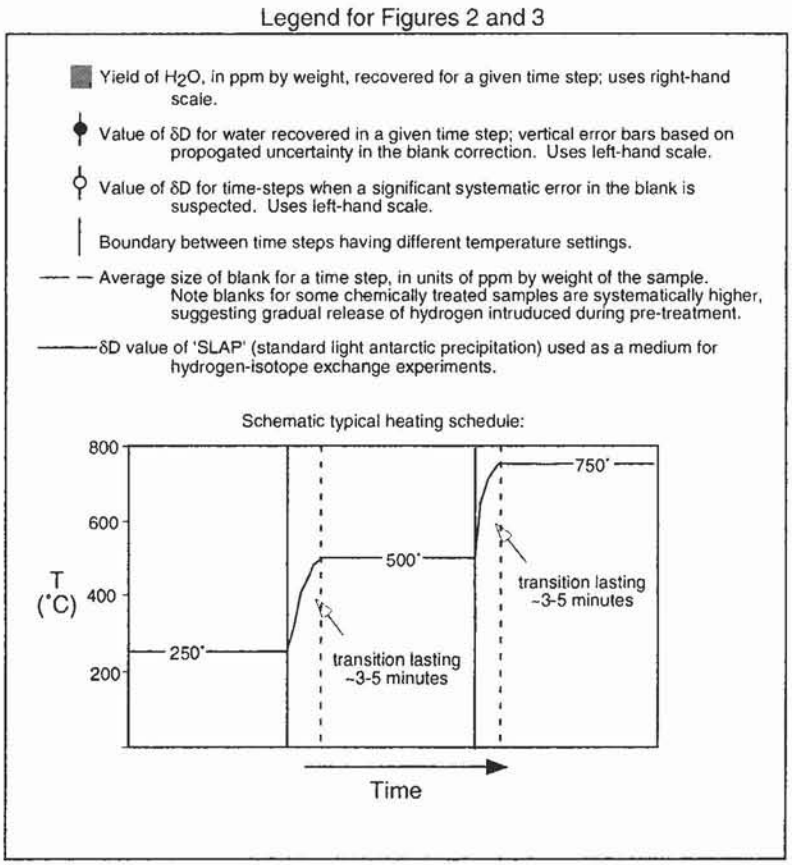


FIG. 2. Results of stepped-heating experiments conducted on untreated portions of ALH 84001. Panels (a), (b) and (c) show representative results for samples weighing between 8 and 30 mg analyzed using the method of Eiler and Kitchen (2001); panel (d) shows the results of Leshin *et al.* (1996) for a 1.1 g sample using conventional methods of vacuum pyrolysis, water reduction and mass spectrometry. See the legend for symbols and details of the heating schedule on the next page.



isotopic composition of the blank was typically about −100 to −120‰ *vs.* SMOW. Error-propagation calculations indicate that when sample water makes up <25% of all of the water measured in a given time step the uncertainty of this correction becomes unacceptably large (tens of per mil or larger) even given the large isotopic "signal" of extraterrestrial water in this sample. Therefore, we have not reported δD values for any time-step during which recovered water was in excess of blank by less than one-third of the blank. Finally, blanks occasionally increase in size briefly after raising the temperature of the step-heating device; if little water is evolved from the sample during this temperature step, this anomaly in the blank can introduce a significant systematic error. We have discriminated all measurements that may be subject to this effect by plotting their δD values as open symbols.

RESULTS

Untreated Samples

Stepped-heating experiments conducted on ~10 mg (about 1–2 mm^3), untreated portions of ALH 84001 yield a reproducible and distinctive variation in the quantity and D/H ratio of water released with increasing temperature; results for three representative experiments illustrating the range of results are shown in Fig. 2 (panels (a), (b) and (c)). These data resemble results of a previous conventional vacuum pyrolysis experiment conducted on a 1.09 g sample of ALH 84001 (Leshin *et al.*, 1996; these data are reproduced for comparison in Fig. 2d). We identify four portions of this pattern: (1) water released at 250 °C and having δD_{SMOW} values (where D/H of SMOW is taken to be 0.00015576; Hagemann *et al.*, 1970) between approximately −100 and 0‰—within the range of terrestrial waters and weathering products; (2) a large quantity of water released during heating through the temperature interval 250 to 500 °C and having a δD_{SMOW} of ~0‰—also within the range of terrestrial materials but somewhat D-enriched compared to most condensed phases on the Earth and possibly reflecting the contribution of a high δD_{SMOW} "martian" component; (3) water released at 500 °C and having δD_{SMOW} values between approximately +400 and +900‰ (generally in the range +600 to +800‰)—strongly D-enriched with respect to natural terrestrial materials and similar to the range of δD values measured for water released by pyrolysis and combustion of ~1 g samples of the nahklites (Leshin *et al.*, 1996); and (4) relatively small amounts of water released at 750 °C and having δD_{SMOW} values that are elevated with respect to natural terrestrial materials but variable and relatively uncertain in D/H ratio, perhaps due to difficulties in measuring such small quantities of water (see "Methods"). We think it likely that this last fraction of water is residual to that released at 500 °C and therefore that it should not be interpreted as a

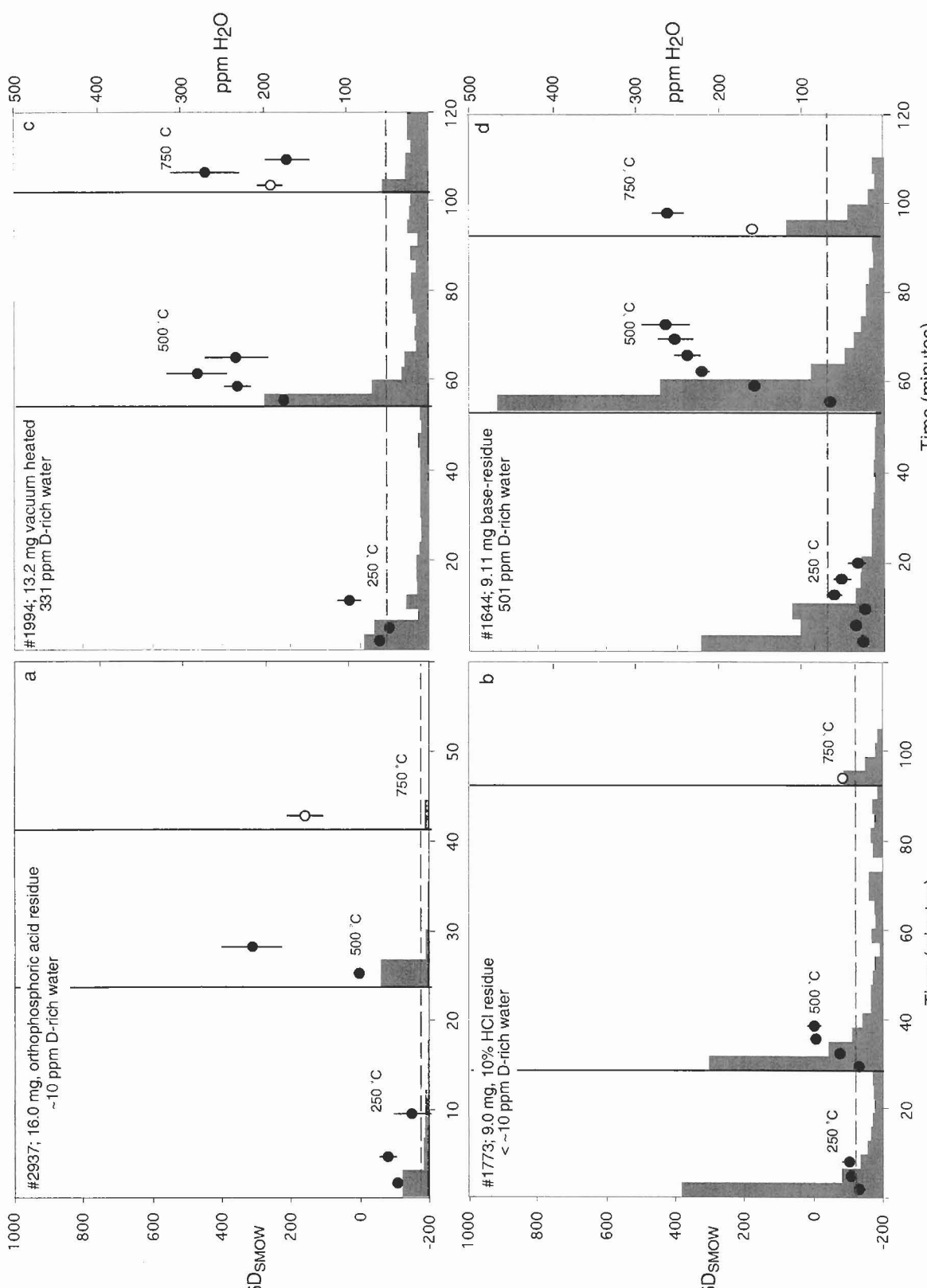


FIG. 3. Results of stepped-heating experiments conducted on variously pre-treated samples of ALH 84001. See legend on previous page for explanation of symbols. See text for discussion of results.

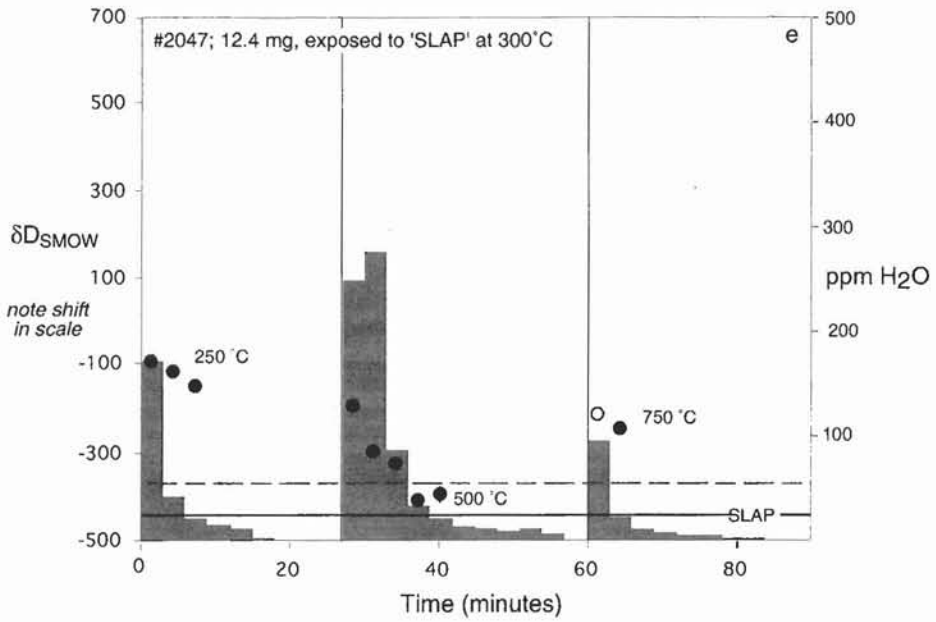


FIG. 3. *Continued.*

second D-rich component. It is noteworthy that most of the water extracted during our experiments is released at temperatures of 500 °C or less—significantly below those at which common magmatic and metamorphic hydrous phases (*e.g.*, micas, amphiboles, phosphates, and glass) liberate water during low-pressure heating in the presence of a carrier gas (Bish and Duffy, 1990). We confirmed this conclusion by conducting stepped-heating experiments on terrestrial micas and amphiboles, establishing that they do not decompose over laboratory timescales at these low temperatures in our apparatus. These temperatures are instead typical of those at which water is released by low-pressure heating of clays, chlorite, organic matter, salts, hydroxides, zeolites and structurally similar but less common hydrous phases (Bish and Duffy, 1990; Gaines *et al.*, 1997).

We find no evidence for water in ALH 84001 that has δD values in excess of about +900‰, in contrast with ion microprobe studies of this sample (Boctor *et al.*, 1998; Sugiura and Hoshino, 2000) that suggest a maximum of up to +1500‰. Assuming that the ion microprobe measurements are not significantly influenced by unaccounted for "matrix effects" (*e.g.*, Valley *et al.*, 1998), this apparent disagreement can be explained in either or both of the following ways: (1) the host(s) of hydrogen having δD values in excess of +900‰ does not dehydrate under the conditions of our experiments (*e.g.*, water-poor silicate glass in this rock does not release significant quantities of hydrogen at the low temperatures and short times of our experiments—see below—and is known from ion probe studies to contain low concentrations of D-rich hydrogen; Boctor *et al.*, 1998; Sigiura and Hoshino, 2000) or (2) hydrogen having δD values in excess of +900‰ is low in abundance and/or distributed approximately evenly through the sample at scales equal to or greater than the sizes of our samples (~1 mm).

One sample (#1172) was re-crushed after a first stepped-heating experiment and subjected to a second stepped-heating experiment; no water in excess of the blank was recovered in this second experiment. We conclude on this basis that all water that can be removed from ALH 84001 by heating to temperatures of 750 °C or lower over the timescales of our experiments is removed in a single stepped-heating extraction.

Pre-Treated Samples

We subjected samples of ALH 84001, also ~10 mg each, to a variety of treatments designed to constrain the physical and chemical properties of hydrous phases, after which the treated samples were examined through stepped-heating experiments like those used to characterize untreated samples. These treatments and their anticipated effects are given below (a–e). Our descriptions of the anticipated effects of heating and exposure to various reagents can be traced to numerous sources on the physical and chemical properties of minerals; Gaines *et al.* (1997) and Bish and Duffy (1990) provide modern syntheses of these data. Note that temperatures of decomposition during stepped-heating experiments can vary with rate of heating and with the presence or absence of an ambient atmosphere (*e.g.*, Robert and Halbout, 1990); our apparatus is most similar to previous studies of thermal decomposition under Ar, N_2 or He flow (Bish and Duffy, 1990).

(a) Exposure to dilute HCl (10% to 1 molar) at temperatures from 25 to 80 °C for times between 2 and 24 h. Many salts (*e.g.*, carbonates, sulfates, and halides) and some hydroxides (*e.g.*, geothite, "limonite") are soluble in dilute, warm HCl, whereas hydrous silicates, including clays, and most refractory organic matter (*e.g.*, kerogen) are not (see also Robert, 1989; Krishnamurthy and Epstein, 1991).

(b) Exposure to concentrated orthophosphoric acid (102% H_3PO_4, prepared by vacuum boiling of commercial 85% H_3PO_4) for 16 h at 50 °C. Carbonates and phosphates are soluble in orthophosphoric acid whereas most silicates and hydroxides are not. Orthophosphoric acid is a weak oxidant as well as an acid and may mineralize certain organics (*e.g.*, amines); it is also highly hydroscopic and may dissolve surface-correlated (*e.g.*, adsorbed) H_2O.

(c) Exposure to concentrated base (equal parts 2 molar NaOH and 30% H_2O_2) for 8 h at 75 °C. Many refractory organic compounds are soluble in warm base whereas most inorganic minerals (silicates and salts) are only weakly soluble or insoluble in such solutions.

(d) Exposure to H_2O of known and extreme δD value (–428.0‰) at temperatures of 25 to 300 °C for times between 2 and 96 h; these experiments test for both solubility in H_2O and rate of H-isotope exchange with co-existing fluid. Halides and certain organics are soluble in warm H_2O whereas most other common hydrous phases are not. Furthermore, hydrous phases containing molecular water (*e.g.*, zeolites) readily undergo D-H exchange with co-existing water at moderate temperatures (room temperature to a few hundred degrees) over timescales of days, whereas hydrous phases in which all hydrogen is bound as members of OH groups (*e.g.*, micas and amphiboles) generally require significantly higher temperatures (~500 °C) and/or far longer times (weeks to months) to isotopically equilibrate with water (Graham, 1981; Cole and Ohmoto, 1986; Savin and Lee, 1988; Cole and Chakraborty, 2001). Similarly, hydrogen in refractory organic matter ("kerogen") generally does not undergo significant isotopic exchange under the conditions of our experiments (*e.g.*, Robert, 1989; Krishnamurthy and Epstein, 1991). However, it is important to note that hydrogen isotope exchange rates between minerals and solutions depend on mineral grain size and in some cases solution composition (Cole and Ohmoto, 1986; Savin and Lee, 1988; Cole and Chakraborty, 2001); therefore exchange experiments on uncharacterized phases can provide guidance for their identification but are less restrictive than the results of acid etches or stepped thermal decomposition experiments.

(e) Vacuum pyrolysis at 150 °C for 16 h. Prolonged vacuum heating can remove water that is adsorbed or weakly bound in zeolites or similarly labile hydrous minerals (Bish and Duffy, 1990; Gaines *et al.*, 1997) but that could potentially contribute to high-temperature stages of our stepped pyrolysis experiments if it is not completely removed by the relatively brief, low-temperature stages of those experiments.

Key results of these experiments are illustrated in Fig. 3 and summarized in the following paragraphs. We have chosen particularly significant experimental results to present in Fig. 3; where appropriate in the accompanying text, we also discuss results of less extreme experiments of a similar type (*e.g.*, acid etches at lower temperatures and/or for shorter times). We have not attempted to interpret subtle variations in abundance or δD of various hydrous components discussed above with reference to Fig. 2 because of the likelihood that they reflect, at least in part, intrinsic variability of the samples; we instead emphasize experiments that effectively remove or radically change the δD of a component that our results described above suggest is always present in untreated samples (*i.e.*, the low δD component released at 250 °C and the high δD component released at 500 and 750 °C):

(1) Both concentrated, warm H_3PO_4 (Fig. 3a) and dilute, warm HCl (Fig. 3b) effectively remove the D-rich components to the release spectra shown in Fig. 2 within several hours (*i.e.*, the abundance of this fraction of hydrogen is reduced from a typical concentration of ~250 ppm in untreated fractions to a concentration of ~10 ppm or less). Acid etches at room temperature or for shorter times reduce the concentration of but do not remove these components, suggesting that loss is a result of time- and temperature-dependent reaction rather than mechanical "washing" of the host phase from the sample (these data resemble results shown in Fig. 2 and are excluded in the interests of brevity; they can be obtained by request from the first author).

(2) Exposure to dilute, warm HCl at temperatures up to 80 °C and for durations up to 24 h has no first-order effect on either the abundance or isotopic composition of D-poor water released at 250 °C and little or no effect on the large quantity of D-poor water released while heating between 250 and 500 °C (Fig. 3b). However, both of these components are greatly reduced in abundance by etching with concentrated H_3PO_4 at 50 °C (Fig. 3a). Few materials are both insoluble in dilute HCl and soluble in concentrated H_3PO_4; the only that we are aware of are phosphates (which generally have dehydration temperatures much higher than those at which D-poor water is released from ALH 84001), certain organic compounds (*e.g.*, amines), and perhaps surface-correlated (*i.e.*, adsorbed) H_2O that may dissolve in hydroscopic, 102% H_3PO_4.

(3) Prolonged vacuum pyrolysis at 150 °C significantly reduces the abundance of water released at 250 °C from untreated samples but has no first-order effect on the higher-temperature, D-rich component(s) of ALH 84001 (Fig. 3c). These results suggest that the D-poor water released at relatively low temperatures contains a component of an adsorbed or weakly-bound phase, such as adsorbed H_2O or volatile organics.

(4) Exposure to base at 75 °C for 8 h has no first-order effect on the water-release spectrum (Fig. 3d), suggesting that the components we identify based on data in Fig. 2 do not include an easily oxidized hydrocarbon.

(5) Exposure to warm, isotopically labeled water changes the isotopic composition of water released from ALH 84001 at 500 °C (D-rich in untreated portions of this sample) toward isotopic exchange equilibrium with that labeled water; near-complete exchange equilibrium is reached in 1 day at 300 °C

(Fig. 3e). In contrast, D-poor water released from ALH 84001 at 250 °C does not change in isotopic composition as a result of this treatment, suggesting it is a hydrocarbon rather than adsorbed H_2O. No hydrous component identified in untreated portions of ALH 84001 is removed (*i.e.*, strongly lowered in concentration) by this treatment; furthermore, the concentration of hydrogen in the sample does not increase as a result of this treatment, suggesting that new hydrous phases are not formed by reaction of anhydrous minerals in the rock with the isotopically labeled H_2O. The water released while heating from 250 to 500 °C is somewhat shifted from its usual δD of ~0 per milliliter in untreated samples toward the δD of the isotopically labeled water to which the sample was exposed. This result is consistent with our speculation described above that this portion of the release spectrum is a combination of low δD water and a first fraction of the component that is released more strongly once the sample has reached 500 °C (usually D-rich; in this case very D-poor). Exposure to isotopically labeled water at lower temperatures (25 to 200 °C) or for shorter times has less pronounced effects on the isotopic composition of hydrous components identified in Fig. 2, suggesting that the changes to the release spectrum we describe are the result of time- and temperature-dependent reaction rather than physical addition of a contaminant (these data resemble results shown in Fig. 2 and are excluded in the interest of brevity; they can be obtained by request to the first author).

Finally, we tested whether water extracted by our stepped-heating experiments included a significant contribution from feldspathic glass by conducting a stepped-heating experiment on ~10 mg of hand-picked glass; the result was not distinguishable from our blank over the full range of temperatures from 250 to 750 °C. We conclude that, although glass may host a small fraction of the hydrogen in ALH 84001 (Boctor *et al.*, 1998; Sugiura and Hoshino, 2000), it contributes little or none to the water extracted by our experiments.

Our results can be compared with the expectations described above to reach the following conclusions about the hosts of hydrogen in ALH 84001:

(1) The host(s) of D-*rich* hydrogen is soluble in dilute HCl and concentrated H_3PO_4, consistent with a hydrous salt (*i.e.*, a mineral containing both large amounts of hydrogen and anionic groups such as Cl^-, CO_3^-, SO_3^-) and inconsistent with silicates, clays, hydroxides, phosphates and most refractory organic matter. Rapid isotopic exchange of this component with co-existing water suggests that most or all of its hydrogen is bound as H_2O rather than as hydroxyl or C–H bonds. The temperature at which this component breaks down (~500 °C) is far higher than the upper stability limits of common hydrous sulfates (*e.g.*, gypsum) and some hydrous carbonates (*e.g.*, natron) and significantly lower than the decomposition temperatures of micas, amphiboles and serpentines; it is within the range of breakdown temperatures determined for hydromagnesite (Rao and Choltan, 1995). All of these properties are consistent with relatively refractory hydrous salts, the most common of which are hydrous carbonates such as hydromagnesite. If hydromagnesite is the host of D-rich hydrogen in ALH 84001, then it must make up ~0.1 wt% of the rock; if contained entirely within carbonate-rich concretions, it would make up ~5% of those concretions (we estimate that white, Mg-rich carbonate rims make up about 10 to 30 vol% of most concretions). However, hydrous salts are diverse (perhaps including some that occur on Mars but not on the Earth) and therefore it is preferable to identify only a class of minerals that are plausible candidates (refractory hydrous salts) rather than specifying a particular mineral (*e.g.*, hydromagnesite). It is also imaginable that this hydrous salt is a solid-solution component in nominally anhydrous carbonates known to be abundant in the rock, although we are aware of no terrestrial examples of magnesiosiderite with a "hydromagnesite" (or similar hydrous carbonate) solid-solution component.

(2) The host(s) of D-*poor* water in ALH 84001 has properties that are not consistent with refractory hydrous silicates (micas, amphiboles, hydrous glass, which do not decompose at sufficiently low temperatures and are not soluble in H_3PO_4), nor with hydrous salts (which are soluble in HCl), nor with most hydrous silicates, clays and hydroxides that contain structural molecular H_2O (which are insoluble in phosphoric acid and generally undergo isotopic exchange over the timescales and at the temperatures of our exchange experiments). Finally, this component is at least partially extracted by prolonged vacuum baking at 150 °C. Some classes of organic matter are consistent with these constraints, although it is peculiar that this component was not efficiently removed by exposure to base and was removed by exposure to phosphoric acid (only a weak oxidant at the temperatures of our experiments). We note that amines are soluble in phosphoric acid and are a plausible host of this hydrogen component; this suggestion could be examined by future studies of the hydrogen isotope geochemistry of compounds removed from this sample by organic solvents. Furthermore, H_2O adsorbed on mineral surfaces should be reduced by low-temperature vacuum heating (Fig. 3c) and may dissolve into hydroscopic solutions like concentrated H_3PO_4, therefore this is also a plausibly candidate for the D-poor component (although this is argued against by the resistance of this component to isotopic exchange; Fig. 3e). Our suggestion that some or all of the D-poor hydrogen in ALH 84001 could come from organic matter is consistent with previous arguments that organics in ALH 84001 are a terrestrial contaminant (Becker *et al.*, 1997; Bada *et al.*, 1998; Jull *et al.*, 1998), although it cannot be taken as a proof of that interpretation (*i.e.*, because it is possible that the martian surface contains organic matter derived from meteorites, which span a wide range of D/H ratios including values comparable to terrestrial organic matter; Robert *et al.*, 2000).

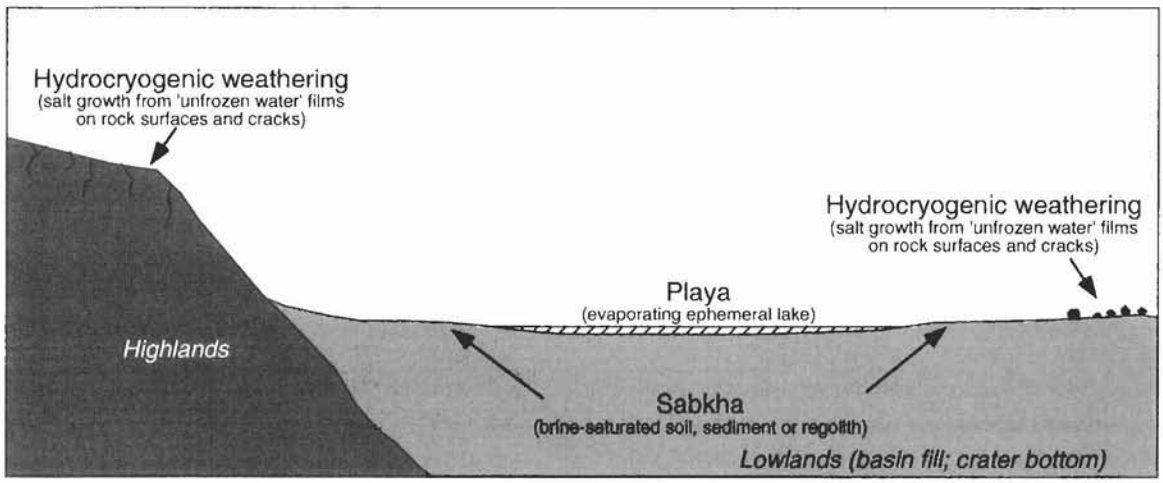


FIG. 4. Schematic illustration of environments on Mars where hydrous salts are likely to form. "Playa": Liquid water migrating from the subsurface, temporarily produced from impact melting of ice or, under conditions not realized today, stable at the martian surface (Baker *et al.*, 1992; Malin and Edgett, 2000) pools in low-lying basins (*e.g.*, impact crater bottoms; erosional basins) and evaporites to form salt pans. "Sabkha": liquid water permeating the shallow subsurface evaporates to form salts trapped in pores of sediment, soil, regolith or fractured rock. "Hydrocryogenic weathering": films of "unfrozen water" (H_2O having properties of liquid below the freezing point of bulk water) coat fractures and exterior surfaces of rocks, transporting solutes and serving as a medium for precipitation of salts.

The hydrous salts we infer host most of the D-rich hydrogen in ALH 84001 have not been identified in this sample by phase-specific diagnostic methods such as electron, x-ray or neutron diffraction (although neither have those methods identified other plausible hosts excepting traces of phlogopite that are too rare to account for a significant fraction of the hydrogen in this rock; Brearley, 2000). We suggest that the apparent inconsistency between our results and previous microscopy studies can be explained by the difficulty in identifying fine-grained (and possibly structurally poorly-defined) phases as components of alteration assemblages. In particular, fine-grained carbonates can be damaged under high-energy electron bombardment and thus it is plausible that carbonate concretions in ALH 84001 contain a component of hydrous salt that could not easily be identified by previous TEM studies (Brearley, pers. comm., 2001). Furthermore, it is possible that hydrous salts in ALH 84001 are distributed on grain boundaries and fractures where they are readily attacked by bulk thermal and chemical treatments but are difficult to identify and characterize by *in situ* microstructural methods. Finally, if hydrous salt is present as a solid-solution component of nominally anhydrous carbonates then it may not be recognizable without detailed structural refinement of those carbonates. A definitive choice among these or other possible explanations will have to await further phase-specific analytical work on alteration assemblages of this rock.

We are aware of only three environments on the Earth where refractory salts such as hydromagnesite commonly form: (1) precipitation from saline, low-temperature (≤50 °C) aqueous solutions exposed at the surface, for instance, in playas; (2) in the immediate subsurface at the interface between water-saturated and water-undersaturated sediment or soil, as in a sabkha environment (*e.g.*, Melezhik *et al.*, 2001); and (3) as a product of "hydrocryogenic" weathering in Antarctic meteorites (Velbel, 1988). We suggest that these are the plausible candidates for environments on Mars in which water was introduced to ALH 84001 as a component of its carbonate-dominated alteration assemblage (Fig. 4). These environments have several features in common: surface temperatures are within tens of degrees of the freezing point of water, parental solutions are solute-rich, the principle acid in solution is carbonic acid, and the environment is arid (*i.e.*, air exposed to the parental solutions is undersaturated with respect to water). This interpretation of our results mirrors recent conjecture that abundant rhombohedral Mg-Fe-Ca carbonates in ALH 84001 were precipitated from aqueous solution in an evaporitic setting (McSween and Harvey, 1998). Finally, we note that conditions consistent with "hydrocryogenic" weathering and/or Sabkha-like evaporite deposit formation plausibly existed in the martian subsurface in the relatively recent past (Bridges and Grady, 2000) and may even persist today (Malin and Edgett, 2000); thus, their record in the oldest martian meteorite is consistent with viewpoint that the near-surface of ancient mars was cold and dry (as today) and supported only intermittent liquid water.

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